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Excitation decay due to incoherent energy transfer: A comparative study by means of an exact density expansion

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In this paper we consider a system of identical, randomly distributed donors, between which incoherent energy transfer takes place, described by coupled rate equations. It is proved, that the well-known diagrammatic series expansion of Gochanour, Andersen, and Fayer for the self-energy, while not an expansion in terms of the density of donors, does in fact imply an exact density expansion for the configuration averaged probability $\rho(t)$, that an initially excited donor will still be excited at time t. Although this diagrammatic expansion has derived its greatest appeal from the search for approximate self-consistent solutions to the generalized diffusion coefficient, the exact density expansion for $\rho(t)$ can also serve very useful purposes. This is demonstrated by a comparative study of model results for $\rho(t)$, whose absolute accuracy or validity can be assessed.

I. INTRODUCTION

In recent years considerable theoretical progress[1–5] has been made in the treatment of incoherent transfer of energy in disordered media. One approach expands on the work of Hahn and Zwanzig,[2] and is due to Gochanour, Andersen and Fayer[3] (GAF). It consists of a diagrammatic series expansion for the Green function solution to the coupled rate equations that describe the migration of excitation energy. Through topological reduction in the series of diagrams involved, GAF arrive at an exact self-consistent equation for the Fourier–Laplace transform of that part of the Green function, which represents the excitation probability on the site of original excitation. Their original work, as well as subsequent applications to more complicated systems,[6,7] then focuses upon the fact, that by truncation of the series of irreducible diagrams beyond a given order m ("m-body" approximation) interesting self-consistent approximate solutions may be obtained, since the diagrammatic expansion does not constitute an expansion in powers of the density, but, to any given order in the diagrams, contains many higher order contributions in the density. Thus one may expect to find surprisingly good approximations to the Green function even for rather low order contributions in the diagrammatic series. In this work we will prove, that, although GAF's expansion does not appear to be a density expansion, and derives its greatest appeal from systematic approximations in terms of the series of diagrams, as indicated above, it nevertheless implies an exact expansion in powers of the density. This will be shown explicitly in Sec. III, after some preliminaries about the model system and the diagrammatic expansion, needed for a self-contained presentation, have been described in Sec. II. In Sec. IV the exact density expansion will be shown to be very useful, for instance, in assessing the validity of a well-known heuristic model for the inclusion of back transfer.[1]

II. THE MODEL SYSTEM AND THE DIAGRAMMATIC EXPANSION

For definiteness, we briefly describe the model, and review those results of the GAF theory that are pertinent for future discussion. Consider a system of volume V (say, a solution) in which energy can be transferred incoherently between N molecules ("donors") randomly distributed with number density n. Each configuration R of the system is characterized by the locations $(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)$ of the donors. In matrix form, the coupled rate equation for the excitation probabilities of the individual donors reads

$$\frac{dp(R;t)}{dt} = -Wp(R;t), \tag{1}$$

where p is a vector with components $p_j(R;t)$ $(j = 1,2,...,N)$, and W is the relaxation matrix due to energy transfer alone (i.e., intramolecular decay has been taken out already). The transfer rates w_{ij}, occurring in W, are symmetric and independent of energy, but with arbitrary dependence on the distance r_{ij} between a pair of donors. In Sec. IV we will discuss definite results for multipolar rates

$$w_{ij} = \frac{1}{\tau}\left(\frac{R_0}{r_{ij}}\right)^s, \tag{2}$$

of which the Förster rate[8] $(s = 6)$ is a well-known example. Here τ is the excitation lifetime of a free molecule, and R_0 the well-known critical transfer distance. The formal solution of Eq. (1) is

$$p(R;t) = \exp[-Wt]\,p(R;0), \tag{3}$$

where the initial condition $p(R;0)$ is determined by the spatial distribution of the initial excitation pulse. The density of excitations $P_R(\mathbf{r},t)$ in a given configuration is defined such that $P_R(\mathbf{r},t)d\mathbf{r}$ is the probability of finding at time t an excited donor in $d\mathbf{r}$ at $\mathbf{r}$. Clearly,

$$P_R(\mathbf{r},t) = \sum_{j=1}^{N} \delta(\mathbf{r}_j - \mathbf{r})p_j(R;t). \tag{4}$$

We are interested in the configuration average $P(\mathbf{r},t)$ of this quantity, that is

$$P(\mathbf{r},t) = \frac{1}{V^N}\int_V d\mathbf{r}_1 ... \int_V d\mathbf{r}_N\, P_R(\mathbf{r},t) \tag{5}$$

for donors of negligible volume, and without correlations between donor positions. The solution can be written, in

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terms of a Green function G, as

$$P(\mathbf{r},t) = \int G(\mathbf{r},\mathbf{r}';t)P(\mathbf{r},0)d\mathbf{r}' \tag{6}$$

with

$$G(\mathbf{r},\mathbf{r}';t) = \frac{1}{n}\left\langle \sum_i \sum_j \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}')[e^{-tW}]_{ij} \right\rangle. \tag{7}$$

Due to the configuration average $\langle \ldots \rangle$ in Eq. (7), G consists of two types of terms only, namely, those with $i=j$ and $i \neq j$. Therefore, we write

$$G(\mathbf{r},\mathbf{r}';t) = G^s(\mathbf{r},\mathbf{r}';t) + G^m(\mathbf{r},\mathbf{r}';t), \tag{8}$$

where

$$G^s(\mathbf{r},\mathbf{r}';t) = \delta(\mathbf{r}-\mathbf{r}')\langle [e^{-tW}]_{11} \rangle \tag{9}$$

and

$$G^m(\mathbf{r},\mathbf{r}';t) = (N-1)\langle \delta(\mathbf{r}_{12} - \mathbf{r} + \mathbf{r}')[e^{-tW}]_{12} \rangle. \tag{10}$$

G^s integrated over a volume $d\mathbf{r}$ at $\mathbf{r}$ gives the configuration averaged probability, denoted by $\rho(t)$, of finding an initially excited donor still in the excited state at time t. Our discussion will focus on this quantity.

GAF have given a diagrammatic expansion *both* for $\hat{G}^s$ *and* $\hat{G}^m$, the Fourier–Laplace transform of G^s and G^m. They derived, in the thermodynamic limit, a self-consistent equation for $\hat{G}^s$, by a topological reduction of the diagrams generated for $\hat{G}^m$. It reads

$$\hat{G}^s(\epsilon) = \{\epsilon + n\tilde{\Sigma}[k=0,\hat{G}^s(\epsilon)]\}^{-1} \tag{11}$$

(GAF, Eq. (65)]. For uniformity, we follow GAF in their notation of $\tilde{\Sigma}$ (which also avoids confusion of the self-energy with summation signs) to indicate that the self-energy Σ depends on ϵ only through $\hat{G}^s(\epsilon)$, as is already clear from the notation in the argument of $\tilde{\Sigma}$. The self-energy can be written as

$$\tilde{\Sigma}[0,\hat{G}^s(\epsilon)] = \sum_{m=2}^{\infty} \tilde{\Sigma}_m[0,\hat{G}^s(\epsilon)], \tag{12}$$

where $\tilde{\Sigma}_m$ is the m-body term [GAF, Eq. (73)]. The m-body term consists of all irreducible diagrams of m circles with the path of arrows starting on one and ending on another circle. Therefore, each diagram contains m-2 field circles. The value of each such diagram d_m is [GAF, Eqs. (42), (43), (44), and (48)]

$$n^{m-1} C_{d_m} [\hat{G}^s(\epsilon)]^{-q_{d_m}}, \tag{13}$$

where $q_{d_m} \geqslant m$, and C_{d_m} is a factor that depends on the specific form of the diagram, *but not on n*.

One then has [GAF, Eq. (74)]

$$n\tilde{\Sigma}[0,\hat{G}^s(\epsilon)] = \sum_{m=2}^{\infty} n^{m-1}[\hat{G}^s(\epsilon)]^{-2} \sum_{d_m} C_{d_m}[\hat{G}^s(\epsilon)]^{-q_{d_m}}. \tag{14}$$

III. EXACT DENSITY EXPANSION FOR ρ

The important point made by GAF is, that Eq. (11) admits interesting approximate solutions by truncation of the series of diagrams [Eq. (14)] at any given order, say, $m=p$ ("p-body approximation") and that approximations of low order, in the expansion in terms of diagrams, may already give surprisingly good results in view of the renormalized vertex contributions. It is clear, that, apart from higher order terms due to these renormalized vertex contributions, the p-body approximation to $n\tilde{\Sigma}$ contains the exact contribution of all unrenormalized diagrams up to (which in the following always means including) order n^{p-1}. However, it is not evident, that GAF's procedure to solve Eq. (11) approximately for $\hat{G}^s(\epsilon)$, by substituting the p-body approximation to $n\tilde{\Sigma}$ as a function of the unknown $\hat{G}^s(\epsilon)$, leads to a result for $\hat{G}^s(\epsilon)$, and hence for ρ, which is exact up to order n^{p-1}. We will now prove, that this is in fact the case.

Assuming the existence of a density expansion for $\hat{G}^s(\epsilon)$, and thus for $\rho(t)$, one can solve the exact self-consistent Eq. (11) in principle by substituting for $\hat{G}^s(\epsilon)$ the power series

$$\hat{G}^s(\epsilon) = \sum_{\lambda=0}^{\infty} \alpha_\lambda n^\lambda \tag{15}$$

with unknown α_λ. By substituting Eq. (15) into Eq. (14) one can formally generate a power series in n for $n\tilde{\Sigma}$, namely,

$$n\tilde{\Sigma} = \sum_{\nu=2}^{\infty} \beta_\nu(\alpha_0,\alpha_1,\ldots,\alpha_{\nu-2}) n^{\nu-1}. \tag{16}$$

One can easily see, that β_ν does not depend on α_μ, with $\mu > \nu - 2$, by determining the lowest order term generated in Eq. (14) by the term of order n^λ in Eq. (15). Equation (11) then becomes

$$\left(\sum_{\lambda=0}^{\infty} \alpha_\lambda n^\lambda\right)\left[\epsilon + \sum_{\nu=2}^{\infty} \beta_\nu(\alpha_0,\ldots,\alpha_{\nu-2}) n^{\nu-1}\right] = 1. \tag{17}$$

The exact solution for α_λ follows straightforwardly by equation of equal powers of n on the left and right-hand side:

$$\left.\begin{aligned} &\alpha_0\epsilon = 1 \rightarrow \alpha_0 = 1/\epsilon, \\ &\alpha_1\epsilon + \alpha_0\beta_2(\alpha_0) = 0 \rightarrow \alpha_1, \\ &\alpha_2\epsilon + \alpha_1\epsilon\beta_2(\alpha_0) + \alpha_0\beta_3(\alpha_0,\alpha_1) = 0 \rightarrow \alpha_2. \\ &\text{etc...} \end{aligned}\right\} \tag{18}$$

In order to evaluate the coefficients α_λ up to $\lambda = k$, one needs to determine the first $k+1$ equations in Eq. (18). Hence one needs to know the functions β_ν for all $\nu \leqslant k+1$.

Suppose now, that instead of the above exact solution, one would construct an approximate solution by terminating the diagrammatic series Eq. (14) for $n\tilde{\Sigma}$ at some $m=p$ ($p \geqslant 2$): the p-body approximation to $n\tilde{\Sigma}$. Then the solution for $\hat{G}^s(\epsilon)$ is, of course, not exact, and can formally be written as

$$\hat{G}^s_{\text{p.b.}}(\epsilon) = \sum_{\lambda=0}^{\infty} \tilde{\alpha}_\lambda n^\lambda, \tag{19}$$

(the subscript p.b. on $\tilde{G}^s_{\text{p.b.}}$, and the $\sim$ on $\tilde{\alpha}_\lambda$ indicate the approximate nature of the solution). The p-body approximation to $n\tilde{\Sigma}$ becomes

$$n\tilde{\Sigma}_{\text{p.b.}} = \sum_{m=2}^{p} n^{m-1}[\tilde{G}^s_{\text{p.b.}}(\epsilon)]^{-2} \sum_{d_m} C_{d_m}[\tilde{G}^s_{\text{p.b.}}(\epsilon)]^{-q_{d_m}} \tag{20}$$

and this can again be expanded in powers of n:

$$n\tilde{\Sigma}_{\text{p.b.}} = \sum_{\nu=2}^{\infty} \tilde{\beta}_\nu(\tilde{\alpha}_0,\tilde{\alpha}_1,\ldots,\tilde{\alpha}_{\nu-2}) n^{\nu-1}. \tag{21}$$

Now, any diagram of the $(p+1)$-body term, which is the first omitted in the p-body approximation, contributes terms proportional to n^p in lowest order [see Eq. (20)]. Therefore, $\tilde{\beta}_\nu$ and β_ν have precisely the same functional dependence on

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their variables for all $\nu \leqslant p$. The self-consistent equation in the p-body approximation reads

$$\left(\sum_{\lambda=0}^{\infty} \tilde{\alpha}_\lambda n^\lambda\right)\left[\epsilon + \sum_{\nu=2}^{\infty} \tilde{\beta}_\nu(\tilde{\alpha}_0,\ldots,\tilde{\alpha}_{\nu-2}) n^{\nu-1}\right] = 1, \quad (22)$$

and this equation can be solved as shown in Eq. (18).

Since β_ν and $\tilde{\beta}_\nu$ are equal for all $\nu \leqslant p$, the equations for $\tilde{\alpha}_\lambda$ with $\lambda \leqslant p-1$ are identical to those for the exact solution. Hence

$$\tilde{\alpha}_\lambda = \alpha_\lambda, \text{ for all } \lambda \leqslant p-1, \quad (23)$$

which proves, that in the p-body approximation, the solution for $\hat{G}^s(\epsilon)$, and consequently $\rho(t)$, equals the exact solution up to terms of order n^{p-1}.

IV. APPLICATION AND DISCUSSION

For donors of negligible volume, in an infinite system of arbitrary dimension Δ, with transfer rates of the general form given by Eq. (2), a scaling argument applies, analogous to the one given by Hemenger and Pearlstein[9] (HP) for $\Delta = 3$ and $s = 6$. In general form, it says, that the average probability ρ of finding an initially excited donor to be still excited at time t, in a system of donor density n, depends on t and n only through

$$T = \hat{n}^{s/\Delta} t/\tau, \quad (24)$$

where $\hat{n} = nV_\Delta R_0^\Delta$ is the average number of donors in a sphere of radius R_0, and V_Δ is the volume of a Δ-dimensional unit sphere. Henceforth ρ is given as a function of T, and further results will be for $\Delta = 3$ and $s = 6$, in which case $T^{1/2}$ is proportional to n. We will now compare various systematic expansions for ρ in terms of $T^{1/2}$, which take the form

$$\rho(T) = \sum_{m=0}^{\infty} a_m T^{m/2}. \quad (25)$$

By virtue of the result of Sec. III, one is now able to make an absolute assessment of their accuracy or validity.

HP[9] have calculated $\rho(T)$ by an expansion in the number of donors with which a given donor, labeled "0", interacts. It turns out, that the contribution, originating from interactions with m donors, is proportional to $T^{m/2}$. The $m = 0$ and $m = 1$ terms were calculated exactly. For higher order terms HP use the intuitive approximation

$$\frac{1}{w_{ij}} = \frac{1}{w_{oi}} + \frac{1}{w_{oj}}, \quad (26)$$

which seems hard to justify on physical grounds. Therefore, *a priori*, the higher order terms in their expansion are not to be trusted. The coefficients a_0 through a_4 are shown in Table I. They are corrected for the orientation factor in the transfer rates, which was included in the HP results, but has been left out of the present results, for the sake of simplicity.

TABLE I. Coefficients in the density expansion $\rho(T) = \Sigma_m a_m T^{m/2}$, as discussed in Sec. IV. a_0 through a_2 for GAF, three body are exact.

Model	a_0	a_1	a_2	a_3	a_4
GAF, two body	1	$-\sqrt{\pi/2}$	0.617	−0.129	0
GAF, three body	1	$-\sqrt{\pi/2}$	0.806	−0.366	0.134
HHB	1	$-\sqrt{\pi/2}$	0.785	−0.328	0.103
HP	1	$-\sqrt{\pi/2}$	0.860	−0.390	0.156

Huber, Hamilton, and Barnett (HHB)[1] have put forward a very appealing heuristic model for $\rho(T)$, in which back transfer is approximately included. Consider a fictitious lattice (of site density ν) of which a small fraction c ($n = \nu c$) is randomly occupied by donors. If, for an arbitrary donor "0" in a particular configuration, there is another donor "1" at close distance, then, because of the uniformity of the distribution, the probability of a second donor being close to 0 is negligible. Appreciable back transfer therefore only occurs between pairs of donors, if they are sufficiently close. To all other donors only transfer, without back transfer, takes place from 0 and 1, respectively, at total rates $w_0' \equiv \Sigma_{j>2} w_{oj}$ and $w_1' \equiv \Sigma_{j>2} w_{1j}$. With the additional assumption,

$$w_0' = w_1', \quad (27)$$

averaging over all configurations becomes simple, and one obtains the HHB solution

$$\rho(c,t) \approx \Pi_{l\neq 0}\left[1 - c + ce^{-w_{0l}t}\cosh(w_{0l}t)\right], \quad (28)$$

where the product is taken over all sites of the fictitious lattice, except the location of donor 0. In the original work of HHB, the factor $\cosh(w_{0l}t)$ is inserted directly into Eq. (28), which makes the solution appear more *ad hoc* than necessary. Indeed, it can simply be derived from the coupled rate equations, with the additional assumption Eq. (27).[10] The latter is very plausible on physical grounds, at least for identical donors and small concentrations. In the continuum approximation, with $\nu \to \infty$, $c \to 0$, and $\nu c = n$ fixed, HHB find

$$\rho(T) = \exp\left[-\sqrt{\pi/2}\,T^{1/2}\right]. \quad (29)$$

The expansion coefficients of Eq. (29) are also given in the Table I.

Finally, we consider the two- and three-body approximation of the GAF expansion, for which GAF have calculated $\hat{G}^s(\epsilon)$. While they were interested in the generalized diffusion constant, we now extract the approximate expression for $\rho(T)$ from their results. By expansion of GAF's two- and three-body solutions for $\hat{G}^s(\epsilon)$ in powers of $1/\epsilon$, and inverse Laplace transformation, one finds in the two-body approximation

$$\rho_2(T) = 1 - \sqrt{\frac{\pi}{2}}\,T^{1/2} + \frac{\pi^2}{16}\,T + \mathcal{O}(T^{3/2}). \quad (30)$$

We know from Sec. III, that the coefficients in the first two terms must be exact. A similar result can be obtained for ρ_3(T); in that case the first three must be exact. All coefficients are given in Table I. In conclusion we make the following observations about the results of Table I.

(i) All models give the exact results for a_0 and a_1.

(ii) The two-body approximation for a_2 differs only by 25% from the exact value (i.e., a_2 in the three-body approximation) which is concrete evidence for GAF's point, that a low order approximation already takes into account a sizeable part of higher order contributions in T.

(iii) The HHB model is remarkably close to the exact results; even a_2 deviates only by 3% from the exact value. Hence the HHB model is indeed a very attractive simple model for the inclusion of back transfer effects.

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(iv) Even the HP results compare rather favorably to the exact results, despite the physically intransparent assumption [Eq. (26)].

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